## §2. Compatibility of Mixed Oxide Ceramics with Liquid Li for Fusion Reactor Blanket Applications

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A self-cooled lithium / vanadium blanket is one of attractive blanket concepts because of its reduced activation, high tritium breeding ratio, accommodation of high heat loads and etc. The primary issue associated with this blanket concept is potentially high MHD pressure drop induced by the liquid lithium flowing through high magnetic fields. In order to reduce this pressure drop to acceptable levels, fabrication of thin insulator coatings to inside of vanadium alloy tubing has been proposed. The coating for Li/V blanket may be one of the most important key-issues, which should be developed to clarify the possibility of Li application itself, because the coating must be minimized chemical corrosion by liquid lithium, chemical corrosion by V alloy tubings, decrease of insulating ability, and erosion by flowing lithium under fusion blanket environments, such as high temperature, severe neutron irradiation, long-term utility and high intensity of magnetic fields, with keeping safety of blanket system. To prevent chemical corrosion by liquid lithium is an important first-step to develop the insulator coatings, because the liquid lithium is one of the strongest reducing materials, which reduse ceramics to a conductive metal phase. Thermodynamic calculations tells us candidate oxide ceramics being stable in liquid lithium will be limited to a small number of a-little-eperienced ceramics, such as, CaO, $Y_2O_3$, MgO, $Er_2O_3$, $Sc_2O_3$ and etc. The compatibility and corrosion mechanisms of these ceramics in liquid lithium, however, should be investigated by the experimental studies, because the thermodynamic calculations cannot show the corrosion rate or effect of impurities in lithium and in the coatings, which have an essential roll for corrosion mechanism. Some experimental results on corrosion by the bulk material testing of these candidates inidicates the coatings should have a higher density and be purified or having more stable impurities in the coatings.

To investigate mixed oxides is considered to be a direction for development of candidate materials, because mixed oxides are always themodynamically more stable than that of the average of each oxide, and they have been sometimes used as a coating material to develop density, micro-structure and advantage of original ceramics. In a viewpoint of chemical corrosion of mixed ceramics, a severe corrosion to a part of oxides may appeare to be broken the whole ceramics. But sometimes we may use stable mixed oxide phase, which should be considered as a new candidate material, even if a part of oxides are unstable in liquid lithium. For example, $CaZrO_3$ is a proper material to investigate effect of the mixed oxide ceramics, because $ZrO_2$ is corrosive while $CaZrO_3$ and CaO may not be corrosive.

In this report, we performed corrosion expriments of bulk ceramics of some mixed oxide phases, and report a possibility to use a mixed oxide phase as a candidate coating materials for Li/V system.

We have tested four mixed oxides phases, $CaZrO_3$, $CaTiO_3$, $MgZrO_3$, and $MgTiO_3$ up to the present, because CaO and MgO are more stable than $Li_2O$ by thermodynamic calculations, while $ZrO_2$ and $TiO_2$ are unstable. In addition, the four mixed oxides phases itself are thermodynamically more stable then $Li_2O$. Bulk compound ceramics of mixed oxides phases immersed in static liquid lithium dissolved in Mo crucibles are installed in stainless steel sample containers under high purity Ar atmosphere and heated up. Only $CaZrO_3$, which is thermodynamically the most stable among these samples, showed a high electrical resistivity after compatibility test at 773 K for 3 months, while the other samples at 673 K for 8 hours are dissolved into lithium or decreased electrical resistivity significantly by the contamination of metal phase reduced by liquid lithium. This indicates that the corrosion was due to the phases themselves in case of $CaTiO_3$, $MgZrO_3$, and $MgTiO_3$ against the thermodynamic predictions, because the corrosion were so severe under lower temperature and in shorter term. Therefore we concentrate on $CaZrO_3$ ceramics to investigate as a example of stable mixed oxides phases in liquid lithium.

Mixed oxides phase sometimes remains un-reacted phases while fabrication, such as $ZrO_2$ in case of $CaZrO_3$. $ZrO_2$, which is thermodynamically unstable in liquid lithium, and composite ceramics 50%$CaZrO_3$-50%$ZrO_2$ are immersed in liquid lithium at 573 K for 3 hours. $ZrO_2$ increased its volume and decreased its electrical resistivity by forming $LiZr_xO_y$, while the composite ceramics disappeared by the immersion test. These may indicate micro $ZrO_2$ phase remained in $CaZrO_3$ phase increased its volume and caused a stress between corrosive $ZrO_2$ phase and stable $CaZrO_3$ phase and, in consequence, whole sample disappeared by changing into micro-pieces. To investigate the effect of $ZrO_2$ remains in the $CaZrO_3$, two more specimen, 75%$CaZrO_3$-25%$ZrO_2$ and 91%$CaZrO_3$-9%$ZrO_2$ are immersed in liquid lithium at 673 K and 773 K for 7 days, as shown in Table 1. The weight and the shape after the immersion test were increased as the increase of $ZrO_2$ fraction in $CaZrO_3$. Therefore, fraction of $ZrO_2$ in the $CaZrO_3$ coatings is an important parameter to be controlled to develop a coating method for $CaZrO_3$.

Table 1 Result on corrosion test of CaZrO3 ceramics containing $ZrO_2$ in liquid lithium.

| Sample | Condition | Weight change | Thickness change |
|---|---|---|---|
| $CaZrO_3$ | 673K, 1 week | +0.2% | -0.3% |
| $CaZrO_3$ | 773K, 1 week | +0.3% | +0.1% |
| 91%$CaZrO_3$-9%$ZrO_2$ | 673K, 1 week | +0.9% | +1.1% |
| 91%$CaZrO_3$-9%$ZrO_2$ | 773K, 1 week | +0.9% | +0.7% |
| 75%$CaZrO_3$-25%$ZrO_2$ | 673K, 1 week | +1.7% | +1.1% |
| 75%$CaZrO_3$-25%$ZrO_2$ | 773K, 1 week | +1.8% | +1.4% |
| 50%$CaZrO_3$-50%$ZrO_2$ | 673K, 1 week | broken | broken |
| 50%$CaZrO_3$-50%$ZrO_2$ | 773K, 1 week | broken | broken |